SPECTRAL STUDIES OF SCHIFF BASES DERIVED FROM AROMATIC ALDEHYDES AND ALIPHATIC AMINES

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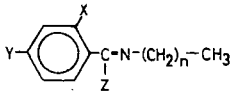
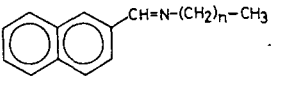
The spectral behaviour of Schiff bases derived from salicylaldehyde, resorcylaldehyde, naphthaldehyde, resacetophenone and *n*-alkylamines (C_{10}, C_{12}, C_{16}, C_{18}) was investigated. From the ultraviolet, infrared and ^1H NMR spectral data it can be established that the alkyl chains have only a small effect on the other part of the molecules.

The electronic spectra of Schiff bases derived from salicylaldehyde and aromatic or aliphatic amines are interesting from the point of view of inter- and intramolecular hydrogen-bond formation, as well as substituent effects. In the solid state the N-salicylidene-anilines have planar [1] or non-planar [2, 3] configurations. With respect to possible deviations from the planar configuration, these compounds can exist with different conformations in solution. The possible tautomeric equilibria are discussed in several papers [4—8]. The aim of the present work is a spectral study of some Schiff bases of aromatic aldehydes and long-chain aliphatic amines (structures I and II).



I.



II.

No.	X	Y	Z	n
1	OH	H	H	15
2	OH	H	H	17
3	OH	OH	H	11
4	OH	OH	H	17
5	OH	OH	CH_3	9
6	OH	OH	CH_3	11
7	OH	OH	CH_3	15
8	OH	OH	CH_3	17

No.	n
9	9
10	11
11	15

Experimental

The Schiff bases were prepared by mixing equivalent amounts of methanolic solutions of the respective aldehydes and amines. The samples were purified by repeated recrystallization from methanol. The m.p. (uncorrected) and analytical data are presented in Table I.

Table I

Analytical data on the Schiff bases

No.	m.p.	C %		H %	
		calc.	found	calc.	found
1	34.2	79.93	79.79	11.37	11.34
2	42.7	80.35	80.31	11.60	11.50
3	52.4	74.71	74.65	10.33	10.18
4	70.8	77.07	77.01	11.13	11.08
5	123.2	74.18	74.08	10.03	10.00
6	111.1	75.19	75.15	10.41	10.34
7	106.3	76.75	76.71	11.00	10.88
8	93.4	77.36	77.25	11.24	11.19
9	47.2	85.35	85.30	9.89	9.85
10	53.8	85.37	85.29	10.28	10.24
11	62.0	85.41	85.36	10.88	10.85

The absorption spectra were measured with a Specord UV—VIS apparatus, using spectrally pure solvents. The ^{1}H NMR spectra were recorded with a Perkin—Elmer R12 60 MHz spectrometer in $CDCl_3$ at room temperature (TMS as internal standard).

The equilibrium constants K of the tautomeric equilibria were calculated as described previously [8].

Results

In the ultraviolet spectral range the aromatic Schiff bases show several well-defined bands which can be assigned to $\pi \rightarrow \pi^*$ transitions [9—13]. The spectra of the compounds studied in this paper may be divided into three types: derivatives of 1) salicylaldehyde, 2) resorcylaldehyde and resacetophenone, and 3) naphthaldehyde.

The spectra of methanolic solution of *1* and *2* show five bands at 398 (ν_1), 314 (ν_2), 276 (ν_3), 254 (ν_4) and 215 (ν_5) nm, with increasing intensity. In cyclohexane or in other non-polar solvents the bands ν_1, ν_2 and ν_4 can be found at almost the same energies, but ν_3 and ν_5 are absent (Fig. 1, Table II) (see *e.g.* [14]).

In mixtures of polar and non-polar solvents the intensities of ν_3 and ν_5 change, depending on the composition of the solvent mixture (Fig. 2). The equilibrium constants K (*e.g.* in the methanol/benzene binary solvent system), calculated on the basis of such a set of curves, are as expected very similar for the two compounds (Table II).

Table II

No.	a)	Spectral data (nm and lg ε) measured in different solvents						^{1}H NMR data[b] δCH_2	δCH_3[c]	δCH_3[d]	δ CHN	K
Hsal—N—CH_3[c]	M	408(3.02)	311(3.65)	282(3.40)	253(4.11)		214(4.44)					
1	M	399(3.38)	314(3.57)	276(3.70)	254(4.09)		216(4.44)	1.32		3.47; 3.58; 3.67	8.27	0.6
	B		315(3.76)									
2	H		318(3.73)		255(4.14)		217(4.44)	1.25		3.43; 3.54; 3.63	8.26	0.7
	M	397(3.40)	315(3.56)	277(3.70)	253(4.06)		217(4.40)					
	B		317(3.89)									
3	M	367(3.94)	303(4.24)	250(3.91)	245(3.92)	232(4.10)	220(4.18)	1.19		3.24; 3.34; 3.43	7.64	5.8
	B		309(4.01)									
4	H		308(3.91)	274(4.24)			221(4.45)	1.26		3.33; 3.44; 3.53	7.74	5.7
	M	367(4.02)	302(4.33)	252(4.00)	246(4.00)	232(4.19)	220(4.27)					
	B		310(4.01)									
5	M	366(4.11)	297(4.32)	250(4.08)	244(4.10)		227(4.37)	1.19	2.21	3.28; 3.39; 3.47		28.0
	B		307(4.01)									
6	M	365(4.18)	296(4.38)	249(4.14)	243(4.15)		227(4.43)	1.18	2.20	3.27; 3.37; 3.48		29.3
	B		307(3.96)									
7	M	366(4.07)	297(4.28)	249(4.02)	244(4.04)		228(4.32)	1.24	2.24	3.34; 3.44; 3.53		17.5
	B		306(3.94)									
8	H		304(4.05)	271(4.18)			227(4.38)	1.23	2.24	3.30; 3.41; 3.50		18.0
	M	365(4.04)	297(4.25)	249(3.99)	244(4.01)		228(4.28)					
	B		306(3.83)									
9	M	293(4.15)	283(4.24)	273(4.14)	251(4.84)	243(4.82)		1.23		3.47; 3.59; 3.69	8.30	
10	M	293(4.09)	282(4.18)	272(4.08)	251(4.78)	244(4.76)		1.21		3.48; 3.59; 3.70	8.30	
11	H	293(4.04)	281(4.17)	272(4.08)	251(4.85)	242(4.85)		1.23		3.50; 3.61; 3.72	8.34	
	M	294(4.04)	283(4.13)	273(4.03)	251(4.74)	244(4.72)						

[a] H: cyclohexane; M: methanol; B: benzene
[b] $CHCl_3$;
[c] $C_6H_4(OH)CH=N-CH_3$;
[d] CH_3 signal;
[e] $-C(CH_3)=N-$ signal

A dramatic change can be observed in the spectra measured in glacial acetic acid, and in methanol containing NaOH or acetic acid (Fig. 3). With increasing acid content two new bands develop (277 and 352 nm) with high and medium intensity, respectively; there is a linear relationship between lg[acid] and ε (Table III).

The NMR spectra of *1* and *2* are similar to those of the other Schiff bases of salicylaldehyde [8]; the methine, methylene and methyl proton signals are observed at 8.27 and 8.26 (singlet), at 1.32 and 1.25, and at 3.58 and 3.54 ppm (triplet), re-

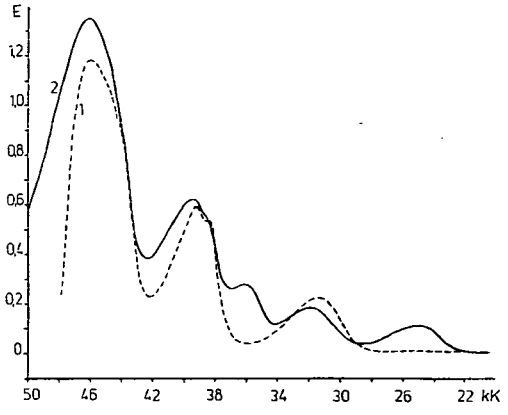


Fig. 1. Electronic spectra of *2*. 1: in cyclohexane; 2: in methanol. $c=4.3\cdot10^{-4}$ M; d=0.1 cm.

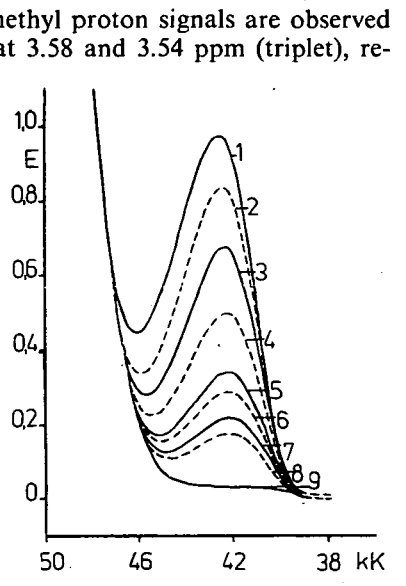


Fig. 2. Absorption spectra of *1* in CH_3OH/C_6H_6 mixtures. $c=5\cdot10^{-4}$ M; d=1.0 cm. 1: in methanol; 2-8 in methanol -benzene mixtures; 2: 0.114; 3: 0.303; 4: 0.683; 5: 1.365; 6: 1.820; 7: 2.578; 8: 3.682; 9: in benzene.

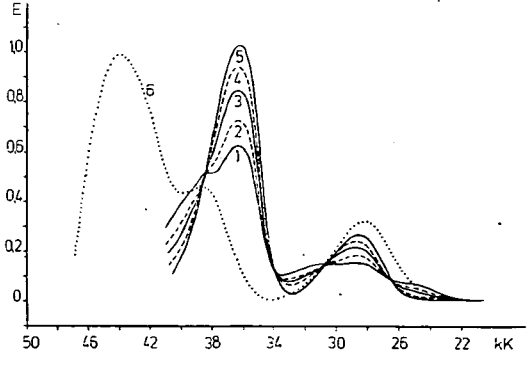


Fig. 3. Absorption spectra of *2* in methanol/glacial acetic acid mixtures. [acid]=1: 0.333; 2: 0.666; 3: 1.332, 4: 2.664 M; 5: in pure acid; 6: in methanol containing 0.02 M NaOH. $c=4.3\cdot10^{-4}$; d=0.1 cm.

Table III

*Spectral change of 1 with the glacial acetic acid concentration in methanolic medium**

[acid]	ε_{275}	ε_{350}
0	6 250	980
0.333	14 550	3 510
0.500	16 100	3 950
0.666	16 900	4 250
1.000	18 500	4 650
1.332	19 700	5 000
2.000	20 900	5 350
2.664	21 950	5 650
⋮	⋮	⋮
14.470	23 950	6 250

* [SB]$=4.3\cdot10^{-4}$ M; d=0.1 cm.

spectively. It can be stated that these bases (*3*—*8* too) exist solely in the phenol-imine form (III) in non-hydroxylic solvents at normal temperatures.

As seen from Table II and Fig. 4, the absorption spectra of *3*—*8* are quite different from those of the two former compounds; the methanolic solutions of *3* and *4*, and *5*—*8*, showed six and five bands, respectively. In glacial acetic acid a new high-intensity band developed at 302 nm, with a shoulder at about 355 nm.

The equilibrium constants calculated for *3* and *4* (5.8 and 5.7), as well as for *5*—*8* (17.5—29.3) are high; this fact suggests that the 5—OH group and the methyl substituent on the azomethine carbon atom favour formation of the quinone-imine tautomer. The significant difference between the *K* values of *5* and *6* and those of *7* and *8* is difficult to interpret. The CHN proton signals of *3* and *4* were observed at 7.64 and 7.74 ppm; for *5*—*8* the —$C(CH_3)$= signals appear at 2.20—2.24 ppm.

The absorption spectra of *9*—*11* are quite similar to those of β-naphthaldehyde or other naphthalene derivatives (Fig. 5); in the range 270—300 nm a band system characteristic of such molecules occurs. In cyclohexane, in glacial acetic acid, or in alkaline methanol the structure of the absorption curves remains almost unchanged; also, the ^{1}H NMR spectra of all three Schiff bases are practically the same (Table II).

Discussion

In the molecules studied there are two chromophores, the phenyl and the azomethine groups [15, 16]. The band of the $n\rightarrow\pi^*$ transition of the unconjugated azomethine group lies at 236 nm, with an extinction coefficient of about 100 [17], but this band is hidden under the more intense bands occurring at around the same energy. The absorption spectra of the compounds studied are essentially slightly modified spectra of the aldehydes in question; *e.g.* in cyclohexane solution the spectra of *1* (Fig. 1) shows bands at 217, 255 and 318 nm, and those of salicylaldehyde (in the same solvent) at 215, 257 and 328 nm. This observation is supported by the

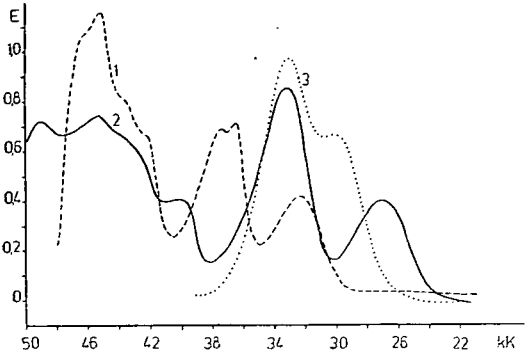


Fig. 4. Spectra of *4*. 1: in cyclohexane; 2: in methanol; 3: in glacial acetic acid. $c = 4.1 \cdot 10^{-4}$; d = 0.1 cm.

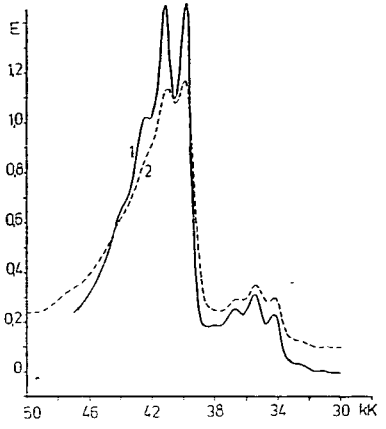
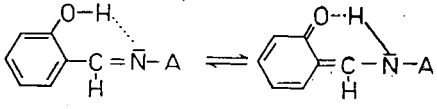


Fig. 5. Absorption spectra of *11*. 1: in cyclohexane; 2: in methanol. $c = 2 \cdot 10^{-4}$ M; d = 0.1 cm.

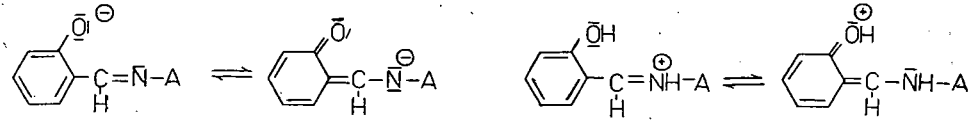
finding [18] that the spectra of $C_6H_5 \cdot CH{=}N{-}CH_3$ and benzaldehyde are very similar. According to several authors (*e.g.* [18]) the 245 nm band of N-benzylimine and probably of our compounds corresponds to the 262 nm band of benzylideneaniline. This band corresponds to a transition to a charge-transfer state in which the phenyl and the azomethine groups act as electron donor and electron acceptor, respectively. Replacing the phenyl group by an alkyl group increases the electronegativity of the nitrogen atom, making the azomethine group a better electron acceptor. We found that these *N*-salicylidene-alkylamines are extremely sensitive to the nature of the solvent. In polar solvents the tautomeric form IV exists pre-



III. IV.

dominantly; due to the conjugation between the azomethine group and the aldehyde ring, two new medium-intensity bands appear, at 276 and 400 nm. In a benzene/methanol binary solvent system the III↔IV equilibrium shifts to the right with increasing concentration of the polar component.

In alkaline and in acidic medium the ionic (V) and the protonated (VI) (the nitrogen lone-pair is localized) forms of the Schiff base molecules are present. In both cases the possible tautomeric forms (V/a and VI/a) must be taken into con-



V. Va. VI. VIa.

sideration, too. On the basis of the spectral change observed it may be stated that the III↔V(VI)↔V/a (VI/a) equilibrium shifts to the right with increasing alkaline and acid concentration.

From the results discussed it is obvious that the long alkyl chains have only a small effect on the other part of the molecules and on their spectra. This is proved by the experimental result that the spectra of the methylamine, 2-aminopropane [14] and octadecylamine derivatives of salicylaldehyde differ only very slightly.

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СПЕКТРАЛЬНОЕ ИЗУЧЕНИЕ ШИФ — ОСНОВАНИЙ, ПОЛУЧЕННЫХ ИЗ АРОМАТИЧЕСКИХ АЛЬДЕГИДОВ И АЛИФАТИЧЕСКИХ АМИНОВ

Й. Часар

Изучены Шиф — основания, полученные из салицилальдегида, резорцилальдегида, нафталальдегида, резацетофенона и алкил-аминов с различной длиной цепи (C_{10}, C_{12}, C_{16}, C_{18}). На оснований УФ, ИК и ^{1}H- ЯМР спектроскопических данных можно прийти к заключению, что алкильные цепи мало влияют на основные свойства изученных молекул.